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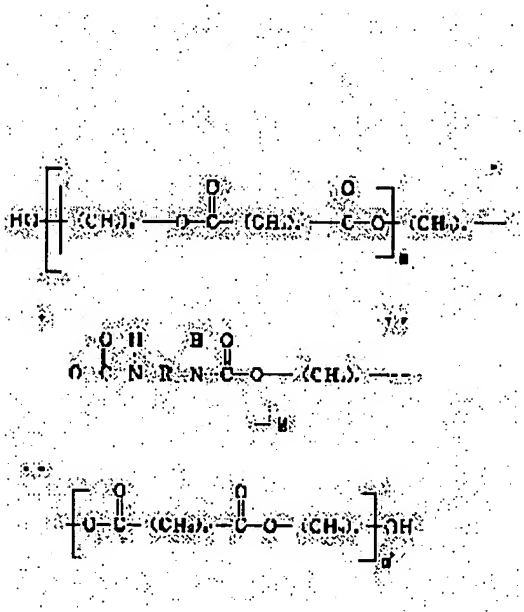
(54) LAMINATED FILM

(57)Abstract:

PURPOSE: To obtain heat seal suitability and biodegradability by a method wherein the unoriented film of the thermoplastic polymer of aliphatic glycol, aliphatic dicarboxylic acid, aliphatic polyester polyol and aliphatic polyester, shown by a formula, is laminated on the biaxially oriented film of thermoplastic polymer of copolymer of polylactic acid.



CONSTITUTION: A laminated film is constituted by a method wherein the thermoplastic polymer unoriented film of aliphatic polyester shown by a formula (here: m, m'≥30, M≥1, n, n'≤10 of even number, R is residue of di-isocyanate) and having the number-average molecular weight of 10000 or more, which can be obtained by reacting polyfunctional isocyanate on aliphatic polyester polyol having a hydroxyl base terminal end obtained by reacting dehydrate reaction and deglycol reaction under the existence or no-existence of aliphatic glycol, aliphatic dicarboxylic acid, small amount of alcohol having polyhydric alcohol of higher than tervalent, polyhydric oxycarboxylic acid or polyhydric carboxyl of higher than tervalent, and the biaxially oriented

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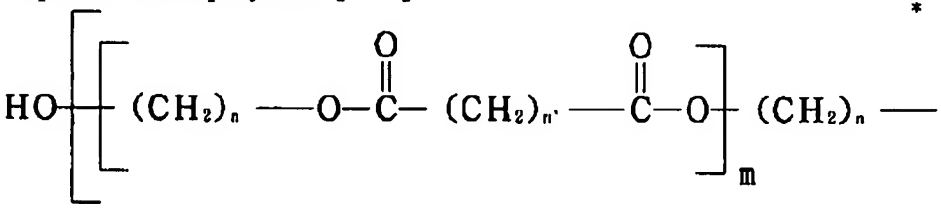
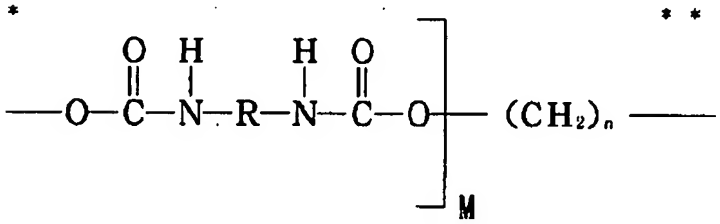
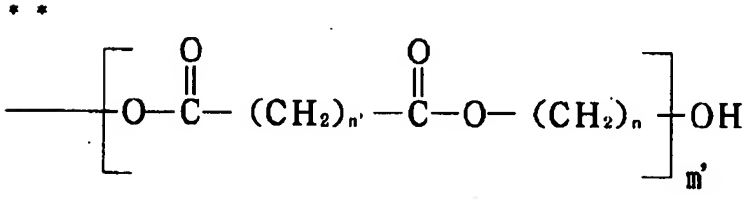
CLAIMS

[Claim(s)]
[Claim 1] (1) Aliphatic series (annular aliphatic series is included) glycol (2) aliphatic-series (annular aliphatic series is included) dicarboxylic acid (or the acid anhydride)
a principal component -- carrying out -- (3) -- a small amount of polyhydric alcohol more than trivalence, multiple-valued hydroxy acid (or the acid anhydride), or the polyvalent carboxylic acid more than trivalence (or the acid anhydride)
With a number average molecular weight of 10,000 or more which polyfunctional isocyanate is made to react to the aliphatic series polyester polyol which has dehydration and the hydroxyl end which is made to carry out a deglycol reaction and is obtained under ****** or nonexistence further, and is obtained aliphatic series polyester [** 1]

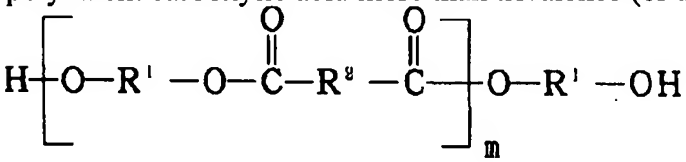






(-- the inside m of a formula, m'>=30, and M>=1 -- it is -- n, the even number of n'<=10, and R -- diisocyanate residue.) -- laminated film characterized by coming to carry out the laminating of the unstretched film of the thermoplastic polymer used as a principal component, and the biaxially oriented film of the thermoplastic polymer which uses the copolymer of polylactic acid or a lactic acid, and hydroxy acid as a principal component.
[Claim 2] (1) Aliphatic series (annular aliphatic series is included) glycol (2) aliphatic-series (annular

aliphatic series is included) dicarboxylic acid (or the acid anhydride)
a principal component -- carrying out -- (3) -- the aliphatic series polyester [** 2] of the number average molecular weight 25,000-70,000 which performs an esterification reaction and is obtained by performing a deglycol reaction under existence of a catalyst in the generated polyester polyol under 180-230-degree C temperature and the high vacuum of 0.005 - 0.1mmHg under existence of a small amount of polyhydric alcohol more than trivalence, multiple-valued hydroxy acid (or the anhydride), or the polyvalent carboxylic acid more than trivalence (or the acid anhydride), or nonexistence



(For the inside of a formula, and m, required polymerization degree, R1, and R2 are the alkylene group of carbon numbers 2-10.) However, branching is also possible when the above-mentioned (3) little component exists. Laminated film characterized by coming to carry out the laminating of the unstretched film of a thermoplastic polymer with which it is expressed and a melt flow rate (JIS law, 190 degrees C, 2.16kg of loads) uses 0.01-100g of resin for /10 minutes as a principal component, and the biaxially oriented film of the thermoplastic polymer which uses the copolymer of polylactic acid or a lactic acid, and hydroxy acid as a principal component.
[Claim 3] Claim 1 characterized by including a metallic-oxide thin film layer at least in one side of said biaxially oriented film, the laminated film of two publications.

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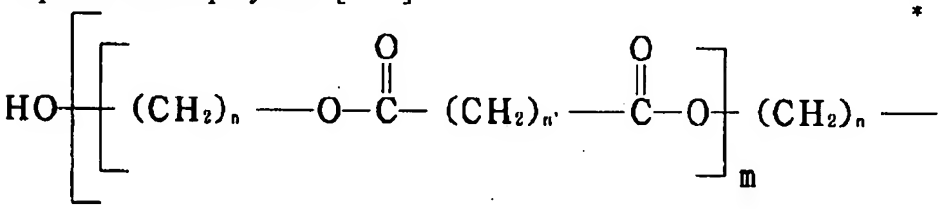

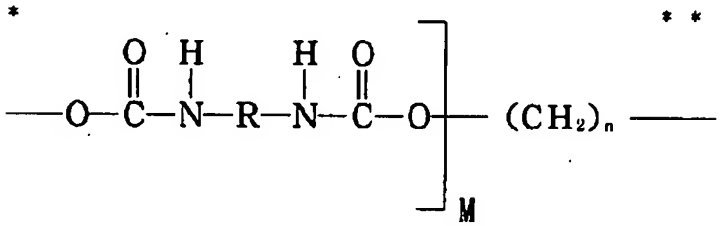

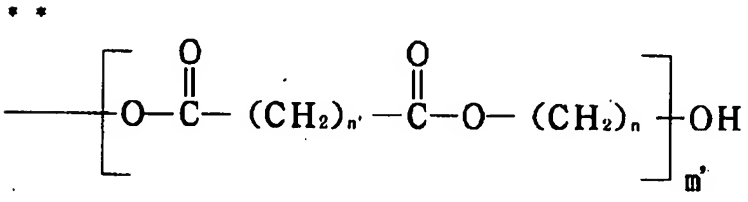

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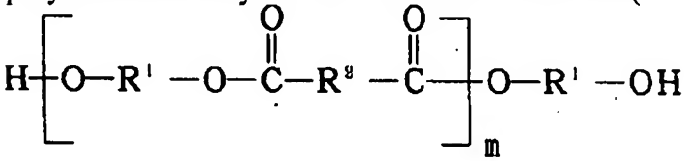

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the package film used for the package fields, such as food, drugs, and a toiletries supply.
[0002]
[Description of the Prior Art] As one of the solutions of the dust trash problem after use of plastics wrapping in recent years, the biodegradable plastic decomposed by the microorganism of a nature attracts attention, and examination is advanced. Furthermore, the attempt made into wrapping using such a biodegradable plastic is performed energetically.
[0003] There are 3-hydroxy butyrate and a 3-hydroxy BARIRETO copolymer, a copolymer of polylactic acid, a lactic acid, and hydroxy acid, etc. as plastics which has such biodegradability.
[0004] Moreover, (1) aliphatic-series (annular aliphatic series is included) glycol and (2) aliphatic-series (annular aliphatic series is included) dicarboxylic acid (or the acid anhydride) are used as a principal component. (3) A small amount of polyhydric alcohol more than trivalence, multiple-valued hydroxy acid (or the acid anhydride), To or the aliphatic series polyester polyol which has dehydration and the hydroxyl end which is made to carry out a deglycol reaction and is obtained under existence of the polyvalent carboxylic acid more than trivalence (or the acid anhydride), or nonexistence with a number average molecular weight of 10,000 or more which polyfunctional isocyanate is made to react furthermore and is obtained aliphatic series polyester (** 1) (the inside m of a formula, m'>=30, and M>=1 -- it is -- n, the even number of n'<=10, and R -- diisocyanate residue --) (It considers as "synthetic aliphatic series system polyester including a urethane bond" hereafter) It is developed.
[0005] Moreover, (1) aliphatic-series (annular aliphatic series is included) glycol and (2) aliphatic-series (annular aliphatic series is included) dicarboxylic acid (or the acid anhydride) are used as a principal component. (3) A small amount of polyhydric alcohol more than trivalence, multiple-valued hydroxy acid (or the anhydride), Or an esterification reaction is performed to the bottom of existence of the polyvalent carboxylic acid more than trivalence (or the acid anhydride), or nonexistence. the aliphatic series polyester (** 2) (the inside of a formula, and m -- required polymerization degree --) of the number average molecular weight 25,000-70,000 obtained by performing a deglycol reaction under existence of a catalyst in the generated polyester polyol under 180-230-degree C temperature and the high vacuum of 0.005 - 0.1mmHg R1 And R2 Alkylene group of carbon numbers 2-10. However, branching is also possible when the above-mentioned (3) little component exists. It is expressed and the thermoplastic polymer (it considers as "the synthetic aliphatic series system polyester which does not include a urethane bond" hereafter) to which a melt flow rate (JIS law, 190 degrees C, 2.16kg of loads) uses 0.01-100g of resin for /10 minutes as a principal component is developed.
[0006] Separately, these biodegradable plastics have some which have what has transparency, heat-sealing nature, etc. However, the heat-sealing fitness which begins transparency, gas barrier nature, contents shelf life, etc., and manufactures the reinforcement as a package bag and a package bag was variety multiple use, and the demand of the function for which wrapping in recent years is asked was

also severe, and, at present, the thing of use to the wrapping of the plastics of biodegradability which satisfies these demands was not especially obtained in the field of soft package material.
[0007]
[Problem(s) to be Solved by the Invention] The place which it is made in order that this invention may solve these troubles, and is made into the technical problem is to offer the laminated film which can be used as a package bag which has biodegradability and has the conventional versatility, such as heat-sealing fitness which begins transparency, gas barrier nature, contents shelf life, etc., and manufactures the reinforcement as a package bag, and a package bag.
[0008]
[Means for Solving the Problem] In order that this invention may solve this technical problem, (1) aliphatic-series (annular aliphatic series is included) glycol (2) aliphatic-series (annular aliphatic series is included) dicarboxylic acid (or that acid anhydride) is used as a principal component. (3) A small amount of polyhydric alcohol more than trivalence, multiple-valued hydroxy acid (or the acid anhydride), To or the aliphatic series polyester polyol which has dehydration and the hydroxyl end which is made to carry out a deglycol reaction and is obtained under existence of polyvalent-carboxylic-acid (or the acid anhydride) ** more than trivalence, or nonexistence with a number average molecular weight of 10,000 or more which polyfunctional isocyanate is made to react furthermore and is obtained aliphatic series polyester (** 1) (the inside m of a formula, m'>=30, and M>=1 -- it is -- n, the even number of n'<=10, and R -- diisocyanate residue --) Or an esterification reaction is performed to the bottom of existence or nonexistence. the aliphatic series polyester (** 2) (the inside of a formula, and m -- required polymerization degree --) of the number average molecular weight 25,000-70,000 obtained by performing a deglycol reaction under existence of a catalyst in the generated polyester polyol under 180-230-degree C temperature and the high vacuum of 0.005 - 0.1mmHg R1 And R2 Alkylene group of carbon numbers 2-10. However, branching is also possible when the above-mentioned (3) little component exists. The laminated film characterized by coming to carry out the laminating of the unstretched film of a thermoplastic polymer with which it is expressed and a melt flow rate (JIS law, 190 degrees C, 2.16kg of loads) uses as a principal component whether to be [0.01-100g] the resin for /10 minutes and ********, and the biaxially oriented film of the thermoplastic polymer which uses the copolymer of polylactic acid or a lactic acid, and hydroxy acid as a principal component is offered. Moreover, the laminated film characterized by including a metallic-oxide thin film layer at least in one side of said biaxially oriented film is offered.
[0009] Hereafter, a drawing explains this invention to a detail. The cross section of a laminated film which is an example of this invention is shown in drawing 1 . The base material film 1 is a biaxially oriented film of the thermoplastic polymer which uses the copolymer of polylactic acid or a lactic acid, and hydroxy acid as a principal component. The thermoplastic polymer which uses polylactic acid or a lactic acid, and hydroxy acid as a principal component has biodegradability, and transparency is excellent.
[0010] Glossiness, a tensile strength property, and thermal resistance of the biaxially oriented film which comes to extend this polymer on two shafts improve further, without spoiling these properties. Although the thickness of the film to be used is limited by the application, 6 micrometers or more 50 micrometers or less are desirable. The reinforcement as a film is not obtained upwards and less than 6 micrometers is difficult to manufacture. Moreover, if thicker than 50 micrometers, time amount will be taken for the chewiness as a film to use it for the application of a flexible packaging material, being too strong for it, and to biodegrade to ****** and coincidence.
[0011] The sealant layer 2 is the unstretched film of the thermoplastic polymer which uses as a principal component synthetic aliphatic series system polyester including a urethane bond, or the synthetic aliphatic series system polyester which does not include a urethane bond.
[0012] The general composition approach of synthetic aliphatic series system polyester including a urethane bond is indicated by JP,4-189822,A. Moreover, this invention persons apply for the general composition approach of the synthetic aliphatic series system polyester which does not include a urethane bond to Japanese Patent Application No. No. 122205 [four to].

[0013] The thermoplastic polymer unstretched film which uses this synthetic aliphatic series system polyester as a principal component is a film which has biodegradability and has the heat adhesive property which was transparent and was excellent. Although it is also possible to use for a package bag as a simple substance film, when the chewiness as a package bag is weak when it uses with a thin film 50 micrometers or less, and it uses with a thick film 50 micrometers or more, transparency and resolvability worsen, anyway, the equipment of the bag manufacture and contents restoration seal by heat sealing becomes special, and versatility is missing with a simple substance film.
[0014] The metallic-oxide thin film layer 3 in another example of this invention shown in drawing 2 is formed in one side even if there are few biaxially oriented films of the thermoplastic polymer which uses the copolymer of polylactic acid or a lactic acid, and hydroxy acid as a principal component.
[0015] As a metallic oxide used for this invention, magnesium oxide, oxidization silicon, an aluminum oxide, the tin oxide, titanium oxide, a zinc oxide, a calcium oxide, etc. are mentioned, and this metallic-oxide thin film layer is formed on this biaxially oriented film by means forming, such as a vacuum deposition method and the sputtering method.
[0016] These metallic-oxide thin film layers have transparency, and have further very high gas barrier nature. 100-3000A is suitable for the thickness of a thin film layer. By 3000A or more, it is easy to produce a crack and exfoliation on the film, and, on the other hand, the stable gas barrier nature is not obtained by 100A or less.
[0017] The copolymer of polylactic acid or a lactic acid, and hydroxy acid At least, although especially the laminating approach of the unstretched film of the thermoplastic polymer which makes a subject the biaxially oriented film of the thermoplastic polymer used as a principal component and this biaxially oriented film that a metallic-oxide thin film layer has in one side, and this synthetic aliphatic series system polyester is not limited The dry laminate method and the wet laminating method using the adhesives of an urethane system are common, and desirable.
[0018]
[Function] Since the laminated film which carried out the laminating of the unstretched film of the thermoplastic polymer which makes synthetic aliphatic series system polyester a subject as a sealant film using the biaxially oriented film of the thermoplastic polymer which uses the copolymer of polylactic acid or a lactic acid, and hydroxy acid as a principal component as a base material film has thermal resistance with this base material film more expensive than the temperature which can heat seal this sealant film, it is stabilized and can perform bag manufacture with a general-purpose bag sealer, and heat sealing of restoration seal of contents. Moreover, a base material film and a sealant film have transparency, and since a base material film also has glossiness, its salability is high, and it can obtain the package bag further disassembled with reclamation, compost, etc. to the inside of soil. Furthermore, the package bag with which high gas barrier nature was also given by preparing the metallic-oxide thin film layer which transparency has at least in one side of a base material film is obtained.
[0019]
[Example]
The biaxially oriented film with a thickness of 15 micrometers was serially obtained from the copolymer of 1:1 of the L-lactic acid of the <example 1> weight average molecular weight 60,000, and a glycolic acid using biaxial-stretching equipment. on the other hand, the mixed reaction of the hexamethylene diisocyanate 1.5 weight section of a coupling agent is carried out to the polyester 100 weight section compounded from the 1,4-butanediol 100 weight section and the succinic-acid 125 weight section -- making (** 1) -- it compounded and number-average-molecular-weight 42000, weight-average-molecular-weight 206000, and melt flow rate 0.5g / polymer for 10 minutes was obtained. The unstretched film with a thickness of 30 micrometers was obtained for this polymer by the cast method. The laminating of the biaxially oriented film and unstretched film which were obtained was carried out by the dry laminate method using the adhesives of an urethane system, and the laminated film was obtained.
[0020] a condensation polymerization reaction is carried out under 220 degrees C and the high vacuum of 0.2 or less mmHgs under existence of a tetraisopropoxy titanium catalyst from the <example 2> 1,4-

butanediol 100 weight section and the succinic-acid 122 weight section -- making (** 2) -- it compounded, number-average-molecular-weight 35000, weight-average-molecular-weight 164000, and melt flow rate 1.1g / polymer for 10 minutes was obtained, and the unstretched film with a thickness of 30 micrometers was obtained for this polymer by the cast method. The laminating was carried out like the biaxially oriented film and example 1 which used this unstretched film instead of and were used in the example 1, and the laminated film was obtained. [the unstretched film used in the example 1]

[0021] Oxidation silicon was vapor-deposited in thickness of about 400A with the vacuum evaporation system by the resistance heating method, and the metallic-oxide thin film layer was formed in one side of the biaxially oriented film used in the <example 3> example 1.

[0022] The laminating of the unstretched film used in the metallic-oxide thin film stratification plane and example 1 of this film was carried out by the dry laminate method with the adhesives of an urethane system, and the laminated film was obtained.

[0023] The result of having performed measurement of the transparency (haze value) of the laminated film obtained in the examples 1-3, oxygen gas transmittance, and steam transmittance is shown in Table 1. Any laminated film of transparency was good, and the laminated film of an example 3 was excellent also in gas barrier nature.

[0024]

[Table 1]

	曇価 (%)	酸素ガス透過度 (cc/m²/day/atm)	水蒸気透過度 (g/m²/day)
実施例1	10	90	25
実施例2	10	100	27
実施例3	12	2	4

[0025] Moreover, the bag which filled up hail with the bag manufacture restoration machine of a vertical pyro mold using these laminated films was created. Heat-sealing temperature at this time was performed at 125 degrees C. The bag in which restoration seal does not have the trouble of heat sealing, either, and any laminated film does not have a wrinkling was obtained. Moreover, when these laminated films were made buried into a 40-degree C compost, it was difficult to disassemble any laminated film six months after, and to check a film.

[0026]

[Effect of the Invention] If the laminated film of this invention is used, it is stabilized, bag manufacture with a general-purpose bag sealer and heat sealing of restoration seal of contents can be performed, it has transparency, glossiness is also excellent, and the package bag further disassembled with reclamation, compost, etc. to the inside of soil can be obtained. Furthermore, the package bag with which high gas barrier nature was also given by preparing the metallic-oxide thin film layer which transparency has at least in one side of a base material film is obtained.

[0027]

[Translation done.]